## JC10 Rec'G PCT/FTO 0 6 MAR 2002

| FORM PTO-1390 U.S. DE (REV. 11-2000)                                     | PARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE   | ATTORNEY'S DOCKET NUMBER   |
|--|--|--|
| TRANSMITTAL LETTER   | TO THE UNITED STATES   | 0475-0205P   |
| DESIGNATED/ELECTE  |  | U.S. APPLICATION NO. (If known, see 37 CER 1.5)  |
| CONCERNING A FILING  | G UNDER 35 U.S.C. 371  | 10/02/03/6   |
| INTERNATIONAL APPLICATION NO.  | INTERNATIONAL FILING DATE  | PRIORITY DATE CLAIMED  |
| PCT/EP00/08568   | September 1, 2000  | September 6, 1999  |
| TITLE OF INVENTION   |  |  |
| ELASTOMER M APPLICANT(S) FOR DO/EO/US                                    | ATERIALS WITH IMPROVED CATALYST  | . COMPONENT  |
| ZECH, Joachim; ECKHARDT, Gur<br>GASSER, O                                | nther; FUHRER, Cornelia; GANGNU<br>swald; KLETTKE, Thomas and WANE   | EK, Erich  |
| Applicant herewith submits to the United States                          |  |  |
| 1. This is a FIRST submission of items conce                             | erning a filing under 35 U.S.C. 371.   |  |
| 2. This is a SECOND or SUBSEQUENT sul                                    | bmission of items concerning a filing under 35 U.S.  |  |
| 3. This express request to begin national of                             | examination procedures (35 U.S.C. 371(f)) at a   | any time rather than delay-  |
|  | applicable time limit set in 35 U.S.C. 371(b) a  |  |
| A  | tion of 19 months from the priority date (Articl   |  |
| 5. A copy of the International Application                               |  | lureati)   |
| 1  | ed only if not transmitted by the International E  | outvau). The second of many flat is a first of the second  |
| b. has been transmitted by the Int                                       | ernational Bureau.  on was filed in the United States Receiving Of   | fice (RO/US)   |
|  | on was filed in the United States Receiving Of<br>he International Application as filed (35 U.S.C  |  |
| a. is transmitted herewith.  | The second of th |  |
| b. has been previously submitted   | under 35 U.S.C. 154(d)(4)  |  |
|  | rnational Application under PCT Article 19 (3:   | 5 U:S.C: 371(c)(3)).   |
|  | red only if not transmitted by the International   |  |
| b. have been transmitted by the I  | The Control of the Co | 700 A 100 A  |
|  | the time limit for making such amendments ha   | as NOT expired.  |
| d. have not been made and will n   | ot be made.  |  |
| 1 to                                  | e amendments to the claims under PCT Article   | e 19 (35 U.S.C. 371(c)(3)).  |
| 9. An oath or declaration of the invento                                 | r(s) (35 U.S.C. 371(c)(4)).  | ing the second s |
|  | ne annexes of the International Preliminary Exa  | amination Report under PCT Article 36  |
| (35 U.S.Č. 371(c)(5)).   |  | a til  |
| Items 11. to 20. below concern document(s)                               | or information included:   | in the second  |
|  | 27 CERTIFICATION P.  | O(c) and International Search Depart   |
| 11. An Information Disclosure Statemen (PCT/ISA/210) with 5 cited docume | t under 37 CFR L97 and 198, Form P10-144 nt(s).  | 9(s), and International Search Report  |
| 12. An assignment document for recordi                                   | ng. A separate cover sheet in compliance with  | 37 CFR 3.28 and 3.31 is included.  |
| 13. A FIRST preliminary amendment.                                       |  |  |
| 14. A SECOND or SUBSEQUENT prel  | imınary amendment.   |  |
| 15. A substitute specification.  | 3.7.<br>   |  |
| 16. A change of power of attorney and/o                                  |  | <u> </u>   |
| ·  | quence listing in accordance with PCT Rule 13  |  |
| ,  | national application under 35 U.S.C. 154(d)(4)   |  |
|  | ge translation of the international application i  | ınder-35 U.S.C. 154(d)(4).   |
| 20. Other items or information:  | - 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1  | ÷  |
| 1) PCT Substitute Letter 2) PCT/IPEA/416                                 | 하는 전환 기가   |  |
| 3) PCT/IPEA/409  |  |  |
| 4) German Search Report  | The state of the s | -  |

# JC13 Rec'd PCT/PTO 0 6 MAR 2002

| - 10.7   | 070376  | INTERNATIONAL APPLICAT                     |                                |                                 |          | ATTORNEY'S DO   | KET NUM          | BER                                     |          |
|--|---|--|--------------------------------|---------------------------------|----------|---|------------------|---|----------|
| 6.3  |   | PCT  | '/EP00/08                      | 3568                            |          |   | 75-0             | 2 <b>0</b> 5P                           | -        |
| 21. The following fees a   | are submitted:  |  |                                | -                               | CAL      | CULATIONS   | S P              | TO USE (                                | ONLY     |
| BASIC NATIONAL F   | EE (37 CFR 1.492(a)(                                      | 1)-(5):                                    |                                |                                 |          |   |                  | ,                                       | -        |
| Neither international pr<br>nor international search   | eliminary examination                                     | fee (37 CFR 1.482)                         |                                |                                 | 1        |   |                  |   |          |
| and International Search   | th Report not prepared                                    | by the EPO or IPO                          |                                | £1 040 00                       | Į        |   |                  |   |          |
| y  | ii report not prepared                                    | by the Li O of Ji O.                       | • • • • • • • • •              | . \$1,040.00                    | 1        |   |                  | -                                       |          |
| International preliminar   | y examination fee (37                                     | CFR 1.482) not paid                        | l to                           | -                               | 1        |   |                  |   |          |
| USPTO but International  | al Search Report prepa                                    | red by the EPO or JI                       | 20                             | \$890.00                        |          |   |                  |   |          |
| Francisco de la constanta de l |   |  |                                |                                 | l        | -   |                  |   |          |
| International preliminar but international search  | y examination fee (37)                                    | CFR 1.482) not paid                        | to USPTO                       |                                 | 1        | -   |                  | -                                       |          |
|  | 100 (37 C1 10 1.443(a)(                                   | 2)) paid to USP (U.                        |                                | . \$740.00                      | l        |   |                  | -                                       |          |
| International preliminar   | y examination fee (37                                     | CFR 1.482) paid to I                       | USPTO -                        | -                               |          | -   |                  |   |          |
| but all claims did not sa  | tisfy provisions of PCT                                   | Article 33(1)-(4).                         |                                | \$710.00                        | 1        |   |                  | -                                       |          |
| Mariana Mariana 1997 .<br>Carana and Mariana 1997 .  |   |  |                                |                                 |          |   |                  |   |          |
| International preliminar and all claims satisfied  | y examination fee (37)                                    | CFR 1.482) paid to U                       | JSPTO                          |                                 |          |   | 1.               |   |          |
| ENTER ADD  | ROPRIATE BA   | CIC PPP ANG                                | OTINITE"                       | \$100.00                        | s        | - 890.00  |                  |   |          |
|  |   |  |                                |                                 |          |   |                  |   |          |
| Surcharge of \$130.00 for months from the earliest   | r furnishing the oath or                                  | declaration later tha                      | ın <u>  20</u>                 | [ ] 30                          | \$       | 130.00  | -                | -                                       |          |
| CLAIMS   | NUMBER FILED  |  | D EVTDA                        | D.A.                            | -        |   | <u> </u>         |   |          |
| Total Claims   | 22 - 20 = _   | - NOMBE                                    | R EXTRA                        | RATE                            | <u> </u> |   | -1L.             |   |          |
| Independent Claims   | 2 - 3 =   |  | 0                              |                                 | \$       | 36.00   |                  | -31                                     | 775      |
| MULTIPLE DEPENDE   |   |  |                                | X \$84.00                       | \$ ;     | 0   | z "              | 3                                       | 1        |
| · ·  |   |  |                                | + \$280.00                      | \$       | 280.00  |                  |   | -        |
| Applicant claims   | TOT   | CAL OF ABOVE                               | CALCUL                         | ATIONS =                        | \$ _ :   | 1,336.00  | <u> </u>         |   |          |
| Applicant claims sm  | all entity status. See 3./                                |  |                                | ove are                         | \$       | 0   |                  |   | -12 .5   |
|  | 2 2   | 4-4  |                                | TOTAL =                         | <b>s</b> | 1:226.00  | -= -             | ***                                     |          |
| Processing fee of \$130.0  | 0 for furnishing the En                                   | glish translation late                     | r than                         | 20 30-                          | JD       | 1,336.00  |                  |   |          |
| months from the earliest   | claimed priority date (                                   | 37 CFR 1.492(f)).                          | ,                              | +                               | \$       | .=- 0   | -                |   | <u> </u> |
| 4  |   | TOTAI                                      | <b>NATION</b>                  | AL FEE =                        | \$       | 1,336.00  | . 4              |   |          |
| Fee for recording the enc  | losed assignment (37 (                                    | FR 1.21(h)). The a                         | ssignment m                    | ust be                          | \$       | 0   | _                | •                                       |          |
| accompanied by an appro  | opriate cover sheet (37                                   |  |                                |                                 |          |   |                  |   |          |
|  |   | TOTAL                                      | FEES ENC                       | CLOSED =                        | \$ -     | 1,336.00  |                  |   |          |
|  | -   | ± =  |                                | Ť                               | A        | mount to be:<br>refunded  | \$               | 7:                                      | 1.17-    |
|  |   | -  |                                | İ                               |          | charged   | \$               |   | - 2      |
| a: A check in the amo  | ount of \$1.33 00 to a                                    |  |                                |                                 |          |   |                  | 7:.                                     |          |
|  | 7.4 he  |  | is enclosed.                   |                                 |          |   |                  | ======================================= |          |
| b. Please charge my l  | Deposit Account. No.                                      | in the a                                   | amount of \$_                  | to cov                          | er the a | bove fees.  |                  |   |          |
| A duplicate copy of  | of this sheet is enclosed                                 |  | = ·- ·                         | - ·                             |          |   |                  |   | ٠,٠      |
| c. The Commissioner overpayment to De  | r is hereby authorized to<br>eposit Account No. <u>02</u> | charge any addition-2448.                  | nal fees whic                  | h may be requ                   | ıred, or | credit any  |                  |   |          |
|  |   |  |                                |                                 |          |   |                  |   |          |
| NOTE: Where an ap 1.137(a) or (b)) must  | propriate time limit the best be filed and granted to     | inder 37 CFR 1.494<br>o restore the applic | f or 1.495 ha<br>cation_to per | is not been me<br>iding status. | t, a pet | tition to reviv   | e (37 C          | FR                                      |          |
| Send all correspondence to:  |   | ,  |                                | ~                               |          |   |                  | c2. l                                   |          |
| Birch, Stewart, Kolase   | ch & Birch, LLP or  | Customer No. 2292                          |                                |                                 | A        |   | 434 <sup>8</sup> | יש                                      |          |
| P.O. Box 747 Falls Church, VA 220  | 140 0747  |  |                                |                                 | [        | $\int \int $ | <b>4</b>         |   |          |
| (703) 205-8000   | 140-0747  |  |                                | ( ) /                           | 7 /      | // ()   |                  |   |          |
|  | ,   |  |                                | $\setminus$ 11                  | 111/6    | Ju. 77  |                  |   |          |
| Date: March 6, 2002  |   |  |                                | By                              | VW       | 100 /   |                  |   |          |
|  | **  | _  |                                | Andrew                          | D. Me    | eikle, #32,868  |                  |   |          |
| /nv  |   | -  |                                |                                 |          |   |                  | • •                                     |          |

PATENT 0475-0205P

IN THE U.S. PATENT AND TRADEMARK OFFICE

Applicant:

ZECH, Joachim et al.

Int'l. Appl. No.: PCT/EP00/08568

Appl. No.:

New

Group:

Filed:

March 6, 2002

Examiner:

For:

ELASTOMER MATERIALS WITH IMPROVED

CATALYST COMPONENET

#### PRELIMINARY AMENDMENT

#### BOX PATENT APPLICATION

Assistant Commissioner for Patents Washington, DC 20231

March 6, 2002

Sir:

following Preliminary Amendments and Remarks respectfully submitted in connection with the above-identified application.

#### **AMENDMENTS**

#### IN THE SPECIFICATION:

Please amend the specification as follows:

Before line 1, insert -- This application is the national phase under 35 U.S.C. § 371 of PCT International Application No. PCT/EP00/08568 which has an International filing dațe September 1, 2000, which designated the United States of America.--

#### IN THE CLAIMS:

Please amend the claims as follows:

- 4. (Amended) Elastomer material according to claim 1, characterized in that the ratio of number of mols of boron in the catalyst component to the number of aziridino equivalents in the mixed preparation is 1:1 to 1:20.
- 5. (Amended) Elastomer material according to claim 1, characterized in that the boric acid complexes are prepared by reaction of boric acid or boric acid derivatives with compounds which contain at least two OH groups or in that the boric acid complexes are prepared by reaction of boric acid esters with compounds which contain at least two OH groups.
- 6. (Amended) Elastomer material according to claim 1, characterized in that the reaction of the boric acid or the boric acid derivative with the OH-functional compounds is carried out before the formulation of the catalyst component and the esterlike boric acid complex is used as a constituent of the catalyst component, or in that the reaction of the boric acid or the boric acid derivative with the OH-functional compounds takes place during the formulation of the catalyst component, or in that the reaction of the boric acid derivative with the

OH-functional compounds takes place during and after the mixing of the catalyst component with the base component.

- 7. (Amended) Elastomer material according to claim 1, characterized in that the formation of the curing-triggering boric acid complex takes place during and/or after the mixing of the catalyst component with the base component from a boric acid derivative of the catalyst component and at least one OH-functional compound with at least 2 OH groups of the base component.
- 8. (Amended) Elastomer material according to claim 1, characterized in that the formation of the curing-triggering boric acid complex takes place during and/or after the mixing of the catalyst component with the base component at least partly from a boric acid derivative, preferably a boric acid ester, of the catalyst component and at least one OH-functional compound of the base component.
- 9. (Amended) Elastomer material according to claim 1, characterized in that a molar ratio between boric acid and the OH-functional compounds of 1: 0.1 to 1: 10, preferably 1: 1 to 1: 4 and particularly preferably of 1: 1.5 to 1: 3 is established.

- 10. (Amended) Elastomer material according to claim 1, characterized in that, as complexing agent for the boric acid, OH-functional organic compounds are used which contain at least one 1,2-dihydroxy and/or at least one 1,3-dihydroxy group.
- 11. (Amended) Elastomer material according to claim 1, characterized in that OH-functional complexing agents are used which have at least one phenolic OH group.
- 13. (Amended) Elastomer material according to claim 1, characterized in that, as complexing agent,  $\alpha$ -hydroxycarboxylic acids and preferably glycolic acid, mandelic acid and benzilic acid are used.
- 14. (Amended) Elastomer material according to claim 1, characterized in that, as complexing agents, compounds with protected and preferably silylated OH groups are used.
- 15. (Amended) Elastomer material according to claim 1, characterized in that several complexing agents are used.
- 16. (Amended) Elastomer material according to claim 1, characterized in that combinations of boric acid complexes with varying structure and composition are used.

- 18. (Amended) Elastomer material according to claim 1, characterized in that the boric acid complexes are used together with other starters and preferably with sulphonium starters.
- 20. (Amended) Use of elastomer materials according to claim 1 for dental modeling, as bite-registration materials or as doubling materials.
- 21. (Amended) Kit which contains the base component and the catalyst component according to claim 1 separately from each other.

#### REMARKS

The specification has been amended to provide a crossreference to the previously filed International Application.

The claims have been amended to remove the improper multiple dependencies in order to place the application into better form prior to examination.

Entry of the above amendments is earnestly solicited. An early and favorable first action on the merits is earnestly solicited.

Attached hereto is a marked-up version showing the changes made to the application by this Amendment.

If necessary, the Commissioner is hereby authorized in this, concurrent, and future replies, to charge payment or credit any overpayment to Deposit Account No. 02-2448 for any additional fees required under 37 C.F.R. § 1.16 or under 37 C.F.R. § 1.17; particularly, extension of time fees.

Respectfully, submitted,

BIRCH, STEWART, KOLASCH & BIRCH, LLP

By WW SW F

Andrew D. Meikle, #32,868

P. d. Box 747
Falls Church, VA 22040-0747

(7/03/) 205-8000

Attachment: VERSIO

ADM/nv

0475-0205P

VERSION WITH MARKINGS TO SHOW CHANGES MADE

(Rev. 02/21/02)

#### VERSION WITH MARKINGS TO SHOW CHANGES MADE

#### IN THE CLAIMS:

The claims have been amended as follows:

- 4. (Amended) Elastomer material according to [one of claims 1 to 3] <u>claim 1</u>, characterized in that the ratio of number of mols of boron in the catalyst component to the number of aziridino equivalents in the mixed preparation is 1 : 1 to 1 : 20.
- 5. (Amended) Elastomer material according to [one of claims 1 to 4] claim 1, characterized in that the boric acid complexes are prepared by reaction of boric acid or boric acid derivatives with compounds which contain at least two OH groups or in that the boric acid complexes are prepared by reaction of boric acid esters with compounds which contain at least two OH groups.
- 6. (Amended) Elastomer material according to [one of claims 1 to 5] claim 1, characterized in that the reaction of the boric acid or the boric acid derivative with the OH-functional compounds is carried out before the formulation of the catalyst component and the ester-like boric acid complex is used as a constituent of the catalyst component, or in that the reaction of the boric acid or the boric acid derivative with the OH-functional compounds takes place during the formulation of the

catalyst component, or in that the reaction of the boric acid or the boric acid derivative with the OH-functional compounds takes place during and after the mixing of the catalyst component with the base component.

- 7. (Amended) Elastomer material according to [one of claims 1 to 6] claim 1, characterized in that the formation of the curing-triggering boric acid complex takes place during and/or after the mixing of the catalyst component with the base component from a boric acid derivative of the catalyst component and at least one OH-functional compound with at least 2 OH groups of the base component.
- 8. (Amended) Elastomer material according to [one of claims 1 to 7] claim 1, characterized in that the formation of the curing-triggering boric acid complex takes place during and/or after the mixing of the catalyst component with the base component at least partly from a boric acid derivative, preferably a boric acid ester, of the catalyst component and at least one OH-functional compound of the base component.
- 9. (Amended) Elastomer material according to [one of claims 1 to 8] claim 1, characterized in that a molar ratio between boric acid and the OH-functional compounds of 1: 0.1 to 1: 10, preferably 1: 1 to 1: 4 and particularly preferably of 1: 1.5 to 1: 3 is established.

- 10. (Amended) Elastomer material according to [one of claims 1 to 9] claim 1, characterized in that, as complexing agent for the boric acid, OH-functional organic compounds are used which contain at least one 1,2-dihydroxy and/or at least one 1,3-dihydroxy group.
- 11. (Amended) Elastomer material according to [one of claims 1 to 10] claim 1, characterized in that OH-functional complexing agents are used which have at least one phenolic OH group.
- 13. (Amended) Elastomer material according to [one of claims 1 to 12] claim 1, characterized in that, as complexing agent,  $\alpha$ -hydroxycarboxylic acids and preferably glycolic acid, mandelic acid and benzilic acid are used.
- 14. (Amended) Elastomer material according to [one of claims 1 to 13] claim 1, characterized in that, as complexing agents, compounds with protected and preferably silylated OH groups are used.
- 15. (Amended) Elastomer material according to [one of claims 1 to 14] <u>claim 1</u>, characterized in that several complexing agents are used.

- 16. (Amended) Elastomer material according to [one of claims 1 to 15] claim 1, characterized in that combinations of boric acid complexes with varying structure and composition are used.
- 18. (Amended) Elastomer material according to [one of claims 1 to 17] claim 1, characterized in that the boric acid complexes are used together with other starters and preferably with sulphonium starters.
- 20. (Amended) Use of elastomer materials according to [one of claims 1 to 18]  $\underline{\text{claim 1}}$  for dental [modelling]  $\underline{\text{modeling}}$ , as bite-registration materials or as doubling materials.
- 21. (Amended) Kit which contains the base component and the catalyst component according to [one of claims 1 to 18]  $\frac{1}{2}$  separately from each other.

- 1 -

#### Elastomer materials with improved catalyst component

The invention relates to improved elastomer materials based on N-alkylaziridino compounds.

In particular, the invention relates to elastomer materials which are characterized by an increased extensibility and are preferably used as dental impression materials, bite-registration materials and doubling materials.

The preparation of elastomer materials based on N-alkylaziridino polyethers and their use in dental materials has been known for a long time. Thus, for example, DE-C-1 745 810 describes the preparation of shaped bodies based on aziridino polyethers.

5

20

25

In the documents DE-C-3 246 654, EP-A-0 421 371 and EP-A-0 110 429, the use of aziridino polyethers in polyether impression materials is described.

It is furthermore known that N-alkylaziridino compounds can cure when exposed to the action of acid-acting compounds (H. Bestian, Methoden der Organischen Chemie [Methods in Organic Chemistry] (Houben-Weyl), XII/1 (1958)). The use of neutral sulphuric acid or sulphonic acid esters as starter substances for the curing of N-alkylaziridino compounds is described in DE-C-888 170.

15 The use of oxonium, ammonium and sulphonium salts as starter substances is proposed in DE-C-914 325.

A summary of the starter substances used for the curing of aziridino compounds is contained in O. C. DERMER, G. E. HAM, "Ethylenimine and other Aziridines" Academic Press (1969).

Accordingly, a large number of compound classes and compounds have proved to be suitable polymerization initiators in principle. In the practical curing of aziridino polyethers, however, it is very difficult to set the desired setting pattern with a sufficiently long processing time and rapid final curing. This object can be achieved by the use of special trisalkylsulphonium salts according to EP-A-0 279 238.

A disadvantage when using sulphonium salts as starter substances is the compounds which form during curing, which have an unpleasant smell.

If strong acids are improperly used as starter substances, there can be an irritant effect on the skin, or corrosion phenomena can occur on metals.

For use, the mechanical properties such as breaking strength and elongation at break of the cured dental materials are of great importance. These properties are in general at a low level when using the known starter substances.

5

The object of the invention is to provided curable preparations containing N-alkylaziridino compounds, during the use of which no unpleasantly smelling compounds form, the use of strong, corrosive acids being avoided and the cured dental materials having improved mechanical properties.

10

15

20

This object is achieved by an improved elastomer material based on N-alkylaziridino compounds, with a base component which contains the aziridino compounds, and with a catalyst component which contains at least one acid-acting compound, both components being mixed before use, characterized in that, as an acid-acting compound of the catalyst component, one or more boric acid complexes are used, which can be obtained by reaction of boric acid and/or a boric acid derivative with at least one OH-functional compound, the OH functions being able to be wholly or partly protected, and this reaction taking place either as an upstream reaction between boric acid and/or a boric acid derivative and at least one such OH-functional compound or during or after the preparation of the catalyst component or by mixing the catalyst component with the base component which then contains one such OH-functional compound.

The elastomer material preferably consists only of the base component and the catalyst component.

The improved elastomer materials according to the invention are used for example as dental impression materials, as bite-registration materials and as doubling materials.

30

The cured materials surprisingly also display markedly improved mechanical properties. Clearly, the mechanical properties, such as breaking strength and

elongation at break of the cured materials, can be influenced through the selection of starter substances.

The boric acid or the boric acid derivatives used as a constituent of the catalyst component are used in a proportion by mass of 0.1 to 100 % of the catalyst compound.

Favourable results with regard to the improvement of the mechanical properties can be achieved if the ratio of the number of mols of boric acid to the number of aziridino equivalents in the cured material is 1: 1 to 1: 20, preferably 1: 1.2 to 1: 10 and particularly preferably 1: 1.5 to 1: 6, the aziridino equivalent mass of the N-alkylaziridino compounds used lying in the range from 500 to 25000 g/equivalent, preferably in the range from 1000 to 8000 g/equivalent and particularly preferably in the range from 2000 to 6000 g/equivalent.

15

10

5

It has long been known that polyol compounds such as sugar, sugar alcohols, sugar acids and uronic acids form ester-like complexes with boric acid. A summary of the analytically relevant results is contained in "Treatise on Analytical Chemistry", Part II, Vol. 10, Wiley, New York.

20

25

30

This complex formation is associated with an increase in acidity and allows the easily-realized alkalimetric titration of boric acid.

Complex formation is however also used in chromatographic and conductimetric analysis processes and in processes for the industrial extraction of boric acid from aqueous mixtures containing same.

Well-examined complexing agents for boric acid with regard to alkalimetric titration are fructose, glycose, mannitol, sorbitol and glycerol; the ionisation constants and the stability constants of the respective complexes are given (W. A. Nasarenko et al., Zaw. Lab. 34 (1968), 257).

Surprisingly it was found that boric acid complexes with OH-functionalized compounds are in a position to effect the curing of N-alkylaziridino compounds at room temperature and at a useful speed, which is mostly not the case with Brönsted acids which possess approximately the same pK<sub>s</sub> value as these complexes.

The discovery that, by using selected polyol boric acid complexes, the level of the mechanical properties can be clearly improved was also wholly surprising.

10 It was furthermore found that both during the formation of the complexes and during the curing of the N-Alkylaziridino polyethers, no unpleasantly smelling compounds form.

Furthermore, the irritant effect of the catalyst component on the skin, for example
when not properly used, and also the corrosive effect on base metals can be
markedly reduced or avoided through the choice of complexing agents.

The reaction products of boric acid with OH-containing compounds, called "polyol boric acid complexes" in simple terms, to be used in the course of the invention are prepared by reaction of boric acid or boric acid derivatives with compounds which preferably contain at least two OH groups, compounds with only one OH group also being able to be used in the complexing.

According to the invention, OH-functional compounds are used which contain at

O II 25 least one and up to 10 OH groups of the general structural formula R1—C—OH R1

5

20

and/or R2, R1, R2 and R3 representing the same or different radicals which are hydrogen, aliphatic, cycloaliphatic, aromatic or araliphatic substituents with 1 to 30 C atoms in each of which one or more C atoms can be replaced by

- 6 -

different and aliphatic, cycloaliphatic, aromatic or araliphatic bivalent radicals with 1 to 30 C atoms.

5

In the complexing agents with two OH groups used according to a preferred version of the invention, these can be present in 1,2 position, in 1,3 position or in a different position if the conformation of these compounds allows the formation of relatively stable complexes. The 1,2 position and the 1,3 position are preferred.

10

25

When using alcohols with more than two OH groups, different positions of these OH groups are possible. The 1,2,3 position such as is present in some sugars is favourable.

15 Complexing agents which have at least one phenolic OH group are used to advantage. In this case, compounds are particularly preferred which also carry at least one other phenolic OH group or an aliphatic OH group and optionally further substituents at the aromatic core.

20 Another preferred group of the complexing agents additionally or exclusively contains carboxylic OH groups. Particularly preferred in this case are compounds which carry an aliphatic OH group in alpha position relative to the carboxyl group.

Typical representatives of the complexing agents for the use according to the invention are:

 Glycerol and its ether or ester derivatives as well as alkoxy-extended glycerols and polyglycerols, such as for example diglycerol, tetraglycerol, glycerol propoxylate,

- 2. Alkylene glycols such as ethylene glycol and propylene glycol and polyalkylene glycols such as for example polyethylene glycol, polypropylene glycol, polyethylene glycol monomethyl ether,
- Mono- and multi-1,2-diols with alkyl radicals or alkylene bridges such as for example 1,2-hexanediol, 1,2-cyclohexanediol, 3-chloropropan-1,2-diol, 1,2-propanediol, 3-mercapto-1,2-propanediol, pinacol, 3-bromopropan-1,2-diol, 1,2-butanediol and 1,2,9,10-tetrahydrodecane,
- Mono- and multi-1,3-diols with alkyl radicals or alkylene bridges such as 1,3-butanediol, 2-ethyl-1,3-hexanediol, 2-ethyl-2-butylpropan-1,3-diol, 1,3-butanediol, 1,3-cyclohexanediol, 1,3-hexanediol, 2,2-diethylpropan-1,3-diol, 2,4-pentanediol, 2-methyl-2-propyl-1,3-propanediol, 2,2-dimethylpropan-1,3-diol, as well as diols such as 1,5-butanediol, 1,6-hexanediol, cis-2-buten-1,4-diol, 2-butin-1,4-diol, and alpha, omega-OH-functionalized polymers such as poly-THF,
- 5. Polyalcohols such as glucose, fructose, lactose, arabinose, ribose, xylose, mannose, galactose, sorbose, xylulose, ribulose, mannitol, sorbitol, maltitol, lactitol, gluconitrilol, pentaerythritol, threitol, erythritol, arabitol,
  - 6. Hydroxycarboxylic acids such as gluconic acid, 2-ketogluconic acid, mannosaccharic acid, mucic acid, glucuronic acid, quinic acid, tartaric acid, ascorbic acid, mandelic acid, 4-chloromandelic acid, lactic acid, glycolic acid, benzilic acid, vinylglucolic acid, citric acid, phenyllactic acid, tropic acid, atrolactic acid, dihydroxyfumaric acid, glycolic acid, quinic acid, hydroxymalonic acid, 2-hydroxysuccinic acid, tartronic acid, salicylic acid,

- Esters of hydroxycarboxylic acids such as gluconic acid ethyl ester, tartaric
   acid diethyl ester, tartaric acid dimethyl ester, tartaric acid dibutyl ester, glycolic
   acid ethyl ester, xylitol dimethacrylate,
  - 8. Dicarboxylic acids such as malonic acid, oxalic acid, fumaric acid, maleic acid, 2,3-dibromosuccinic acid, succinic acid, glutaric acid,
- 9. Phenolic compounds such as pyrocatechol, 4-tert.-butylpyrocatechol, 3,5-ditert.-butylpyrocatechol, pyrogallol, salicylic alcohol, 3-methoxypyrocatechol,

2,3-dihydroxynaphthalene, 5-bromosalicylic alcohol, 5-chlorosalicylic alcohol, 4-chlorosalicylic alcohol, 3-chlorosalicylic alcohol, 3,5-dichlorosalicylic alcohol,

The use of several such OH-functional compounds is possible and can be expedient to establish special properties such as for example a desired chronological curing pattern.

The molar ratio between boric acid and the OH-functional compounds can be varied within a wide range from 1:0.1 to 1:10, the range from 1:1 to 1:4 being preferred.

10

15

30

The optimum ratio for each case depends on the necessary concentration in each case and the solubility of the complex, the equilibrium position and the effect of an excess of complexing agent on the properties of the dental materials.

Instead of boric acid, boric acid derivatives such as for example boric anhydride, borates and boric acid  $C_{1-18}$ , preferably  $C_{2-4}$  esters can be wholly or partly used.

Furthermore the use of the starters according to the invention for the curing of the N-alkylaziridino compounds is also possible in combination with other known starter substances such as Brönsted acids or sulphonium salts, the described negative effects of the last-mentioned starters being reduced and their positive effects, such as for example good adjustability of the curing pattern being used.

There are various variants for the realization of the use according to the invention of the boric acid complexes as starter substances of polyether curing.

According to the first variant, the reaction is carried out before the formulation of the catalyst component, and the ester-like boric acid complex is used as a constituent of the catalyst component.

The preparation of the complex takes place in per se known manner, for example with the addition of toluene as entrainer for the water produced by esterification.

According to a second variant, the complexing of the boric acid is effected by mixing of boric acid or a boric acid derivative with the OH-functionalized compound(s) during the formulation of the catalyst component, the water produced by esterification either remaining in the catalyst component or being wholly or partly removed by suitable measures such as for example a vacuum treatment of the catalyst component.

5

20

25

30

Normally the formulation of the catalyst component takes place at temperatures in the range from 20 to 50°C, the application of higher temperatures can be expedient in accelerating the complexing or in establishing the desired water content.

When using the first and second variants, the base component can optionally also contain a neutral or basic-acting boric acid derivative such as for example alkali salts of boric acid or trialkyl esters of boric acid.

According to a third variant, the complex starting the curing is formed only after the mixing of the catalyst component with the base component, the catalyst component preferably containing the boric acid or a boric acid derivative and the base component the complexing agent.

According to a particular version of the third variant, the boric acid is present in the catalyst in a complexed or esterified form; after mixing with the base component, a recomplexing takes place.

According to a further version of the third variant, the complexing of the boric acid is effected by one or more compounds in which the OH groups of these compounds are derivatized. Upon mixing of the two components, the reactive boric acid complexes are formed.

A derivatization of the OH groups can be achieved for example by esterification, etherification or silylation, silylation being preferred.

The silylated complexing agents can be used both in the base component and in the catalyst component.

The listed variants and their versions can also be used in combination with each other. Such combinations can prove to be favourable in increasing the storage stability of the catalyst and base components.

To achieve specific mechanical properties or to achieve a desired setting pattern, it can be expedient to use combinations of boric acid complexes with varying structure and composition.

Usually, the catalyst components contain according to the preferred first and second variant:

- 15 (A) 0.1 to 100 wt.-% of at least one boric acid complex, optionally in an excess of complexing agent,
  - (B) 0 to 95 wt.-% of at least one inert diluent,
  - (C) 0 to 80 wt.-% of modifiers, including fillers, dyes, pigments, thixotropic agents, flow-improvers, polymeric thickeners, surfactants, stabilizers, polymerizationretarding compounds, odorous substances and flavourings,

the wt-% data being related in each case to the overall mass of the catalyst component;

and the base components:

- 25 (D) 5 to 100 wt.-% of a mixture of N-alkylaziridino compounds with aziridino equivalent masses of 500 to 25000 g/equivalent, preferably in the range from 1000 to 8000 g/equivalent and particularly preferably in the range from 2000 to 6000 g/equivalent,
  - (E) 0 to 95 wt.-% of at least one inert diluent,

(F) 0 to 80 wt.-% of modifiers, including fillers, dyes, pigments, thixotropic agents, flow-improvers, polymeric thickeners, surfactants, stabilizers, polymerizationretarding compounds, odorous substances and flavourings,

the wt-% data being related in each case to the overall mass of the base component;

and the components being stored separately and being mixed together for processing in a catalyst component to base component ratio of 5 : 1 to 1 : 20, preferably 1 : 1 to 1 : 10.

10

15

25

30

5

There can be used, as inert diluents according to constituents (B) and (E), polyether polyols, such as for example polypropylene glycols or mixed polyetherols with tetrahydrofuran and/or ethylene oxide and/or propylene oxide units, polyester polyols, such as for example polycaprolactone diols and polycaprolactone triols, polycarbonate diols, aliphatic esters, oils, fats, waxes, aliphatic hydrocarbons, araliphatic hydrocarbons and also mono- or multifunctional esters of multivalent acids such as for example phthalic acid, adipinic acid or citric acid or esters or amides of alkylsulphonic acids and arylsulphonic acids.

Constituent (B) or (E) is used in quantities of 0 to 95 wt.-%, preferably 10 to 90 wt.-% and particularly preferably 40 to 85 wt.-%, relative to the overall weight of the catalyst component or the base component.

As compounds according to the constituents (B) or (E), organic compounds can be used which hydrophobize the total mixture and belong to completely different compound classes.

Good results are achieved with hydrocarbons with 6 to 30 C atoms which are dissolved in the base component or can be incorporated in stable fine-particle form. The hydrocarbons can be aliphatic and/or aromatic and also olefinic and be present in branched and/or linear form.

Typical examples are polypropylene oils or polyisobutylene oils. Aromatic hydrocarbons such as for example polyphenylene compounds, dibenzyltoluene and dibenzylphenylmethane are used to advantage.

Waxy compounds with ester structures can also be used. Typical representatives of this compound class are the ester waxes such as are marketed for example by Hoechst under the name Hoechst-Wachs E; F; X 22.

Modifiers can be added to the catalyst component and also to the base component in a broad concentration range according to constituents (C) or (F). Constituents (C) or (F) are used in quantities of 0 to 80 wt.-%, preferably 0 to 50 wt.-% and particularly preferably in each case 15 to 40 wt.-%, relative to the overall weight of the catalyst component or base component.

These modifiers are mostly fine-particle fillers such as alumosilicates, silicic acids, quartz powder, wollastonite, mica powder and diatomaceous earth as well as dyes and pigments, the addition of which makes possible a better assessment of the mixed product and reduces the danger of confusion, thixotropic agents such as finely-dispersed silicic acids and other additives influencing the flow behaviour, such as polymeric thickeners, furthermore surfactants for establishing the flow-on behaviour and also odorous substances and flavourings.

As constituent (D) of the base component, mixtures of N-alkylaziridino compounds are used, the aziridino equivalent masses being able to be varied from 500 to 25000 g/equivalent and the number of N-alkylaziridino groups being able to be varied between 1 and 4 per molecule.

25

30

Preferably mixtures of N-alkylaziridino polyethers are used which consist of at least up to 60 % of polyether compounds which carry at least two aziridino groups. According to another preferred version of the invention, mixtures of N-alkylaziridino polyethers are used which consist of at least up to 5 % of polyether compounds which contain at least 3 aziridino groups.

Polyether basic bodies that can be used are those with tetrahydrofuran and/or ethylene oxide and/or propylene oxide units.

Preferably, the mixture of the N-alkylaziridino polyethers consists of mixed-5 polyether derivatives of ethylene oxide and tetrahydrofuran, incorporated in a molar ratio of 1:2 to 1:5, preferably 1:3 to 1:4.

Constituent (D) is used in concentrations of 5 to 100 wt.-%, preferably 20 to 70 wt.-% and particularly preferably 30 to 60 wt.-%, relative to the overall weight of the base component.

To establish the desired setting pattern, the preparations according to the invention according to constituent (C) or (F) can contain at least one curing-retarding compound. In principle, amine or alkaline substances retard the curing of the N-alkylaziridino compounds and can be used for this purpose.

Thus DE-A1-197 534 61, to the full contents of which reference is made here, describes the use of 0.0005 to 50 wt.-% of soluble and/or fine-particle alkaline-earth and/or alkali metal compounds.

20

15

10

Thus for example solutions of lithium compounds, such as lithium hydroxide or lithium carbonate, can be added to the catalyst component and/or the base component. The use of lithium carboxylates is also possible.

The two-component preparations according to the invention based on N-alkylaziridino compounds can be used, depending on the composition of the catalyst component and the base component, for the gluing of substrates, for sealing, coating and casting.

30 However, the preparations according to the invention are preferably used for the modelling of objects, models with accurate details being obtained with the preparations according to the invention due to their excellent flow-on behaviour.

The preparations according to the invention are used to particular advantage in dental modelling and in dental doubling.

In dental modelling, the good flow-on behaviour on the moist tooth and the moist gum as well as the insensitivity of the precision of the modelling vis-à-vis saliva and blood proves to be of great advantage.

5

10

15

20

In dental doubling, the good flow-on behaviour on hydrophilic plaster surfaces and the good wettability of the obtained doublings with plaster pulp or admixed investment compound formulations is advantageous.

The dosing of the two components can be carried out by sight, for example via the so-called strand-length comparison, by weight, via pre-dosed pack units and subsequent manual admixing, from double-chambered cartridges with static mixing tube or by means of volume dosing systems with downstream static or dynamic mixers.

A high mixing quality is required to achieve optimum results. On the other hand, the tolerance of the mixing ratio is in general relatively high and can for example cover the range from 0.75 to 1.25 : 5, with a preset catalyst component to base component ratio of 1 : 5, without use-restricting property changes being ascertained.

The invention is described in more detail by the following examples without being limited thereby.

#### **Examples**

5

10

20

#### 1. Preparation and testing of impression materials

With the help of laboratory kneaders, the catalyst components described in Table 1 were prepared on 100-g scale. The preparation of the base components which are described in Table 2 was carried out on 500-g scale.

Table 3 lists the mixtures which were examined using the catalyst components described in Table 1 and the base components described in Table 2, in the weight ratio indicated in each case. The mixtures were prepared by smoothing onto the mixing block within 30 seconds and used to determine the properties also listed in Table 3.

The mouth-removal time was able to be determined as the average value of each of 3 impressions from 3 different subjects in the form of a complete upper-jaw impression.

All mixtures of examples 1 to 10 according to the invention (Table 3) yielded impressions which were not sticky after removal from the mouth and were characterized by a very good design sharpness.

The individual components and also the mixtures did not display any unpleasant or noticeable odour.

#### 2. Preparation and testing of doubling materials

The catalyst components described in Table 4 were prepared on 100-g scale by mixing the organic components and incorporating the fillers with the help of a dissolver and homogenizing in a laboratory kneader.

5

15

The preparation of the base components described in Table 5 took place analogously on 100-g scale, the organic thixotropic additive used (Thixatrol ST) being dissolved at 55° - 60° before the incorporation of the fillers.

The properties, obtained upon mixing of the components in the weight ratio 1:1, of the doubling materials are listed in Table 6.

The doubling materials according to invention examples 11 to 16 were characterized by an excellent design sharpness, a very good flow-on behaviour on hydrophilic plaster surfaces and an excellent wetting of the obtained doublings with plaster pulp or the admixed investment compound.

#### 3. Preparation and testing of bite-registration materials

The catalyst components described in Table 7 and the base components described in Table 8 were prepared on 100-g or 500-g scale in laboratory kneaders.

Table 9 contains the characterization of the mixtures which were prepared by smoothing onto the mixing block within 25 seconds.

25

20

Furthermore, Table 9 contains the processing time of the mixtures obtained at 23° C, the mouth-removal time, each measured from the start of mixing and the shore A hardness after 24 hours.

The bite-registration materials according to invention examples 17 to 20 were characterized by a very high precision and were easy to cut and mill.

<u>Table 1</u>
Composition of the catalyst components for dental impression materials

| Constituent   | Name of the catalyst components |       |       |       |       |       |  |  |  |
|---|---------------------------------|-------|-------|-------|-------|-------|--|--|--|
|   |                                 |       | wt.   | -%    |       |       |  |  |  |
|   | AM-K1                           | AM-K2 | AM-K3 | AM-K4 | AM-K5 | AM-K6 |  |  |  |
| Boric acid  | 3.72                            | 3.57  | 3.81  |       | 1.10  | 3.70  |  |  |  |
| Salicylic alcohol   | 16.00                           | 15.70 | 21.00 |       | 5.90  |       |  |  |  |
| Mandelic acid   |                                 |       |       |       |       | 19.60 |  |  |  |
| Reaction product of boric acid with salicylic alcohol in the molar ratio 1 : 2                                      |                                 |       |       | 15.30 | 12.70 |       |  |  |  |
| Precipitation silicic acid (Sipernat D17)   | 20.30                           | 21.50 | 20.00 | 21.00 | 23.70 | 20.20 |  |  |  |
| Statistical mixed polyetherdiol, prepared from ethylene oxide and propylene oxide with a molar mass of 3200 g / mol |                                 | 58.53 | _     |       | 25.30 |       |  |  |  |
| Polypropylene oxide diol with a molar mass of 2000 g / mol  |                                 |       | 54.41 | 63.00 | 30.60 | 55.80 |  |  |  |
| Polypropylene oxide diol with a molar mass of 4000 g / mol  | 59.28                           |       |       |       |       |       |  |  |  |
| Lithium hydroxide   |                                 |       | 0.08  |       |       |       |  |  |  |
| Coloring paste, red   | 0.70                            | 0.70  | 0.70  | 0.70  | 0.70  | 0.70  |  |  |  |

<u>Table 2</u>
Composition of the base components for dental impression materials

| Constituent  |       | wt%   |       |
|--|-------|-------|-------|
|  | AM-B1 | AM-B2 | AM-B3 |
| Mixture of bisaziridino polyethers with an average imino equivalent mass of 3100, prepared from a polyetherdiol which is composed of ethylene oxide and tetrahydrofuran units in the molar ratio 1: 3.5 with a cyclic polyether content of 0.27% | 55.70 | 58.11 | 54.97 |
| Diatomaceous earth<br>(Celatom MW 25)  | 10.69 | 11.50 | 14.00 |
| Hydrogenated vegetable oil   | 13.91 | 12.51 | 14.72 |
| Dibenzyl toluene   | 17.80 | 9.08  | 9.41  |
| Statistical mixed polyetherdiol, prepared from ethylene oxide and propylene oxide with a molar mass of 3200 g / mol  |       | 6.90  | _     |
| Polypropylene oxide diol with a molar mass of 2000 g / mol   |       | —     | 5.00  |
| Coloring paste, grey   | 1.90  | 1.90  | 1.90  |

- 19 -

Elastomer materials according to the invention using the catalyst components according to Table 1 and base components according to Table 2 and determined properties Table 3

|                                    |       |       |       | lnv   | ention ex | Invention examples-No. | O     |       |       |       |
|------------------------------------|-------|-------|-------|-------|-----------|------------------------|-------|-------|-------|-------|
|                                    | -     | 2     | က     | 4     | 2         | 9                      | 7     | 8     | 6     | 10    |
| Catalyst component                 | AM-K1 | AM-K1 | AM-K2 | AM-K2 | AM-K2     | AM-K3                  | AM-K4 | AM-K5 | AM-K5 | AM-K6 |
| Base component                     | AM-B1 | AM-B2 | AM-B1 | AM-B2 | AM-B3     | AM-B1                  | AM-B3 | AM-B1 | AM-B2 | AM-B1 |
| Mixing ratio<br>(by weight)        | 1:4.7 | 1:5.4 | 1:4.9 | 1:5.1 | 1:4.6     | 1:5.0                  | 1:5.1 | 1:5.2 | 1:4.8 | 1:5.0 |
| C:B                                |       |       |       |       |           | ·                      |       |       |       |       |
| Start of curing at 23° C (seconds) | 120   | 120   | 130   | 125   | 135       | 150                    | 125   | 145   | 140   | 40    |
| Mouth-removal time (seconds)       | 260   | 245   | 280   | 270   | 290       | 275                    | 280   | 250   | 240   | 120   |
| Elongation at break / %            | 235   | 255   | 246   | 257   | 242       | 285                    | 320   | 380   | 360   | 140   |
| Tensile strength / MPa             | 1.65  | 1.75  | 1.89  | 1.85  | 1.95      | 1.84                   | 1.90  | 2.01  | 2.10  | 1.35  |
| Shore A hardness after 24 h        | 48    | 52    | 49    | 51    | 53        | 49                     | 50    | 48    | 51    | 20    |

<u>Table 4</u>
Composition and viscosity of the catalyst components for doubling materials

| Constituent  |             |       | wt.   | %     |       |       |
|--|-------------|-------|-------|-------|-------|-------|
|  | DM-K1       | DM-K2 | DM-K3 | DM-K4 | DM-K5 | DM-K6 |
| Boric acid   | 0.65        | 0.63  | 0.66  |       | 0.65  | 0.72  |
| 4-tertbutylpyrocatechol  | 3.49        | 3.42  | 3.55  |       | _     |       |
| Pyrocatechol, silanized with dichlorodimethylsilane                          |             |       |       |       | 7.00  |       |
| Reaction product of boric acid with pyrocatechol in the molar ratio 1 : 1.95 |             |       |       | 2.40  |       |       |
| 1,6-hexanediol   | 4.00        | 4.50  |       |       | 4.50  |       |
| L-(+)-tartaric acid diethylester   |             | 6.00  |       |       |       |       |
| cis-1,4-butenediol   | <del></del> |       | 5.86  |       |       |       |
| Glycolic acid  |             | _     |       |       |       | 0.8   |
| Glycerol   |             |       |       |       | _     | 1.65  |
| Alkyl sulphonic acid ester of phenol (Mesamoll)                              | 11.86       | 5.45  | 29.22 | 13.60 | 9.85  | 18.83 |
| Phthalic acid polyester<br>(Ultramoll PP)                                    | 66.00       | 66.00 | 47.00 | 70.00 | 66.00 | 66.00 |
| Precipitation silicic acid (Sipernat D10)                                    |             |       | 4.90  |       | _     |       |
| Precipitation silicic acid (Sipernat 22S)                                    | 10.00       | 10.00 | 8.80  |       |       | 6.00  |
| Pyrogenic silicic acid<br>(HDK H 2000)                                       | 4.00        | 4.00  |       | 14.00 | 12.00 | 6.00  |
| Coloring pigment, yellow (Thermoplastgelb 084F)                              | _           |       | 0.01  |       |       |       |
| Viscosity of the catalyst component / mPa·s                                  | 3020        | 2480  | 1980  | 2250  | 2530  | 2620  |

<u>Table 5</u>
Composition and viscosities of the base components for doubling materials

| Constituent   |       | wt%     |       |
|---|-------|---------|-------|
|   | DM-B1 | DM-B2   | DM-B3 |
| Mixture of bisaziridino polyethers with an average imino equivalent mass of 3120, prepared from a polyetherdiol which is composed of ethylene oxide and tetrahydrofuran units in the molar ratio 1: 3.4 | 40.00 | 39.70   | 45.00 |
| Diatomaceous earth<br>(Celatom MW 25)   | 16.00 | 15.30   | 10.00 |
| Dioctyl adipate<br>(Plastomoll DOA)   | 38.24 | 42.4998 | 40.50 |
| Block mixed polyether<br>(Synperonic PE / L 121)  | 5.00  |         | 2.50  |
| Modified castor oil derivative (Thixatrol ST)   | 0.75  | 1.00    |       |
| Modified layered silicate<br>(Bentone SD-3)   |       | _       | 2.00  |
| Coloring paste, white (Lithopone)   |       | 1.50    |       |
| Dye, purple<br>(Makrolex Violett B)   | 0.01  | _       |       |
| Dye, blue<br>(Thermoplast Blau 684)   |       | 0.0002  |       |
| Viscosity of the base component / mPa·s   | 3460  | 3020    | 3950  |

<u>Table 6</u>
Tested mixtures and determined properties for doubling materials

|                                     | Invention examples-No. |       |       |       |       |       |
|-------------------------------------|------------------------|-------|-------|-------|-------|-------|
|                                     | 11                     | 12    | 13    | 14    | 15    | 16    |
| Catalyst component<br>(cf. Table 4) | DM-K1                  | DM-K2 | DM-K4 | DM-K3 | DM-K5 | DM-K6 |
| Base component<br>(cf. Table 5)     | DM-B1                  | DM-B1 | DM-B1 | DM-B2 | DM-B1 | DM-B3 |
| Mixing ratio by weight              | 1:1                    | 1:1   | 1:1   | 1:1   | 1:1   | 1:1   |
| Start of curing / seconds           | 195                    | 675   | 135   | 315   | 240   | 215   |
| End of curing/ seconds              | 520                    | 1800  | 420   | 855   | 780   | 760   |
| Shore A hardness after 24 hours     | 23                     | 19    | 18    | 22    | 16    | 25    |
| Tensile strength / N                | 13.5                   | 15.4  | 9.5   | 16.7  | 10    | 14.1  |
| Elongation at break / %             | 131                    | 192   | 127   | 201   | 160   | 170   |

<u>Table 7</u>
Composition of the catalyst components for bite-registration materials

| Constituent   | Name of the catalyst components |       |       |  |  |
|---|---------------------------------|-------|-------|--|--|
|   |                                 | wt%   |       |  |  |
|   | вм-к1                           | BM-K2 | вм-кз |  |  |
| Reaction product of boric acid and salicylic alcohol in the molar ratio 1 : 2.1       |                                 | 10.40 | 12.15 |  |  |
| Reaction product of boric acid and 5-bromosalicylic alcohol in the molar ratio 1:1.95 | 19.80                           | 4.70  | 2.75  |  |  |
| Salicylic alcohol   |                                 |       | 3.85  |  |  |
| Polypropylene oxide diol with a molar mass of 2100 g / mol                            | 53.75                           | 57.85 | 55.80 |  |  |
| Precipitation silicic acid<br>(Sipernat D17)  | 25.70                           | 26.30 | 24.70 |  |  |
| Coloring paste, white   | 0.75                            | 0.75  | 0.75  |  |  |

<u>Table 8</u>
Composition of the base components for bite-registration materials

| Constituent  | Name of the base component |       |  |  |
|--|----------------------------|-------|--|--|
|  | wt.                        | -%    |  |  |
|  | BM-B1                      | BM-B2 |  |  |
| Mixture of bisaziridino polyethers with an average imino equivalent mass of 3100, prepared from a polyetherdiol which is composed of ethylene oxide units and tetrahydrofuran units in the molar ratio 1: 3.6 and has a cyclic ether content of 0.31 | 58.10                      | 25.00 |  |  |
| Mixture of bisaziridino polyethers with an average imino equivalent mass of 1600, prepared from a polyetherdiol which is composed of ethylene oxide units and tetrahydrofuran units in the molar ratio 1: 3.4 and has a cyclic ether content of 0.38 |                            | 29.75 |  |  |
| Diatomaceous earth<br>(Celatom MW 25)  | 34.00                      | 39.27 |  |  |
| Hydrogenated vegetable oil   | 5.00                       | 4.20  |  |  |
| Dibenzyl toluene   | 2.90                       | 1.68  |  |  |

#### Table 9

Bite-registration materials according to the invention using the catalyst components according to Table 7 and the base components according to Table 8 and determined properties

|                                     | In    | Invention examples-No. |       |         |  |  |  |
|-------------------------------------|-------|------------------------|-------|---------|--|--|--|
|                                     | 17    | 18                     | 19    | 20      |  |  |  |
| Catalyst component<br>(cf. Table 7) | BM-K1 | BM-K2                  | BM-K2 | вм-кз   |  |  |  |
| Base component (cf. Table 8)        | BM-B1 | BM-B1                  | BM-B2 | BM-B2   |  |  |  |
| Mixing ratio (by weight) C: B       | 1:5.0 | 1:5.3                  | 1:4.8 | 1 : 5.0 |  |  |  |
| Processing time / seconds           | 50    | 45                     | 70    | 80      |  |  |  |
| Mouth-removal time / seconds        | 140   | 120                    | 160   | 150     |  |  |  |
| Shore A hardness (after 24 h)       | 71    | 73                     | 81    | 83      |  |  |  |

5

10

15

20

PCT/EP00/08568

- 26 -

2<sup>nd</sup> August 2001

#### Patent claims:

1. Elastomer material based on N-alkylaziridino compounds with a base component which contains the aziridino compounds and with a catalyst component which contains at least one acid-acting compound, both components being mixed before use, characterized in that as acid-acting compound of the catalyst component, one or more boric acid complexes are used which can be obtained by reaction of boric acid and/or a boric acid derivative with at least one OH-functional compound, the OH functions being able to be present wholly or partly protected, and this reaction being carried out either as an upstream reaction between boric acid and/or a boric acid derivative and at least one such OH-functional compound or during or after the preparation of the catalyst component or by mixing the catalyst component with the base component which then contains at least one such OH-functional compound, and the at least one OH-functional compound containing at least one and up to 10 OH groups and having the general structural formula

R1—C—OH R3—C—OH
R1—C—OH and/or R2 , R1, R2 and R3 representing the same or different radicals which display hydrogen, aliphatic, cycloaliphatic, aromatic or araliphatic substituents with 1 to 30 C atoms in each of which one or more C

R1' and R2' being the same or different and aliphatic, cycloaliphatic, aromatic or araliphatic bivalent radicals with 1 to 30 C atoms.

25 2. Elastomer material according to claim 1, characterized in that the curing of the aziridino compounds takes place through boric acid complexes

AMENDED PAGE IPEA/EP

- 27 -

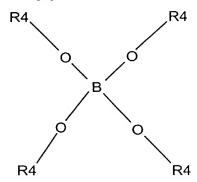
which correspond to the following general structural formula,

ART 30 AMOT

5

10

15



in which the substituents R4 can be different or the same or bridged with each other and R4 can mean: hydrogen, an aliphatic, cycloaliphatic, aromatic or araliphatic radical with 1 to 30 C atoms and one or more C atoms can be replaced by

in which R5 is hydrogen or C1 to C12 alkyl and R4 and also R5 can carry one or more halogens, -CN, -OH, -SH, -COOH, -COO( $C_{1-18}$  alkyl), -NO<sub>2</sub>, SO<sub>3</sub>H, alkylthio-, keto- and also aldehyde groups as substituents.

- Elastomer material according to one of claims 1 to 2, characterized in that the catalyst component contains 0.1 to 100 wt.-% of boric acid complexes with OHfunctional compounds optionally in an excess of these OH-functional compounds.
- 4. Elastomer material according to one of claims 1 to 3, characterized in that the ratio of number of mols of boron in the catalyst component to the number of aziridino equivalents in the mixed preparation is 1 : 1 to 1 : 20.

AMENDED PAGE IPEA/EP

ART 34 AMOT

5

10

15

20

25

- 5. Elastomer material according to one of claims 1 to 4, characterized in that the boric acid complexes are prepared by reaction of boric acid or boric acid derivatives with compounds which contain at least two OH groups or in that the boric acid complexes are prepared by reaction of boric acid esters with compounds which contain at least two OH groups.
- 6. Elastomer material according to one of claims 1 to 5, characterized in that the reaction of the boric acid or the boric acid derivative with the OH-functional compounds is carried out before the formulation of the catalyst component and the ester-like boric acid complex is used as a constituent of the catalyst component, or in that the reaction of the boric acid or the boric acid derivative with the OH-functional compounds takes place during the formulation of the catalyst component, or in that the reaction of the boric acid or the boric acid derivative with the OH-functional compounds takes place during and after the mixing of the catalyst component with the base component.
- 7. Elastomer material according to one of claims 1 to 6, characterized in that the formation of the curing-triggering boric acid complex takes place during and/or after the mixing of the catalyst component with the base component from a boric acid derivative of the catalyst component and at least one OH-functional compound with at least 2 OH groups of the base component.
- 8. Elastomer material according to one of claims 1 to 7, characterized in that the formation of the curing-triggering boric acid complex takes place during and/or after the mixing of the catalyst component with the base component at least partly from a boric acid derivative, preferably a boric acid ester, of the catalyst component and at least one OH-functional compound of the base component.
- 9. Elastomer material according to one of claims 1 to 8, characterized in that a molar ratio between boric acid and the OH-functional compounds of 1:0.1 to 1:10, preferably 1:1 to 1:4 and particularly preferably of 1:1.5 to 1:3 is established.

AMENDED PAGE IPEA/EP

10. Elastomer material according to one of claims 1 to 9, characterized in that, as complexing agent for the boric acid, OH-functional organic compounds are used which contain at least one 1,2-dihydroxy and/or at least one 1,3-dihydroxy group.

5

ART 34 AMOT

- 11. Elastomer material according to one of claims 1 to 10, characterized in that OH-functional complexing agents are used which have at least one phenolic OH group.
- 12. Elastomer material according to claim 11, characterized in that, as complexing agent, pyrocatechol or 2,3-dihydroxynaphthalene is used, the phenyl radical(s) optionally being able to contain further substituents such as alkyl, halide, alkyl ester, alkyl ether, carboxyl and/or hydroxyl, or in that salicylic alcohol is used as complexing agent, the phenyl radical optionally being able to contain further substituents such as alkyl, halide, alkyl ester, alkyl ether, carboxyl and hydroxyl.
  - 13. Elastomer material according to one of claims 1 to 12, characterized in that, as complexing agent, α-hydroxycarboxylic acids and preferably glycolic acid, mandelic acid and benzilic acid are used.
  - 14. Elastomer material according to one of claims 1 to 13, characterized in that, as complexing agents, compounds with protected and preferably silylated OH groups are used.

25

- 15. Elastomer material according to one of claims 1 to 14, characterized in that several complexing agents are used.
- 16. Elastomer material according to one of claims 1 to 15, characterized in that combinations of boric acid complexes with varying structure and composition are used.

ANT 34 ARMOR

10

15

20

25

- 17. Elastomer material according to claim 16, characterized in that, as complexing agent, 4-tert.-butylpyrocatechol is used in combination with an aliphatic OH-functional compound.
- 18. Elastomer material according to one of claims 1 to 17, characterized in that the boric acid complexes are used together with other starters and preferably with sulphonium starters.
  - 19. Process for the preparation of elastomer materials based on N-alkylaziridino compounds with a base component which contains the aziridino compounds and with a catalyst component which contains at least one acid-acting compound, both components being mixed before use, characterized in that as acid-acting compound of the catalyst component, one or more boric acid complexes are used which can be obtained by reaction of boric acid and/or a boric acid derivative with at least one OH-functional compound, the OH functions being able to be present wholly or partly protected, and this reaction being carried out either as an upstream reaction between boric acid and/or a boric acid derivative and at least one such OH-functional compound or during or after the preparation of the catalyst component or by mixing the catalyst component with the base component which then contains at least one such OH-functional compound and the at least one OH-functional compound containing at least one and up to 10 OH groups and having the general

- 31 -

Many State Whood

O; O; R1' and R2' being the same or different and aliphatic, cycloaliphatic, aromatic or araliphatic bivalent radicals with 1 to 30 C atoms.

- 5 20.Use of elastomer materials according to one of claims 1 to 18 for dental modelling, as bite-registration materials or as doubling materials.
  - 21. Kit which contains the base component and the catalyst component according to one of claims 1 to 18 separately from each other.

#### Elastomer materials with improved catalyst component

#### <u>Abstract</u>

5

10

15

The invention relates to elastomer materials based on N-alkylaziridino compounds with a base component which contains the aziridino compounds and with a catalyst component which contains at least one acid-acting compound, both components being mixed before use, characterized in that, as acid-acting compound of the catalyst component, one or more boric acid complexes are used which can be obtained by reaction of boric acid and/or a boric acid derivative with at least one OH-functional compound, the OH functions being able to be present wholly or partly protected, and this reaction being carried out either as an upstream reaction between boric acid and/or a boric acid derivative and at least one such OH-functional compound or during or after the preparation of the catalyst component or by mixing the catalyst component with the base component which then contains at least one OH-functional compound. The elastomer materials are preferably used as dental impression materials, bite-registration materials and doubling materials.

Attorney Docket No. 0475-205P

PLEASE NOTE: YOU MUST COMPLETE THE FOLLOWING

#### BIRCH, STEWART, KOLASCH & BIRCH, LLP

P.O. Box 747 • Falls Church, Virginia 22040-0747 Telephone: (703) 205-8000 • Facsimile. (703) 205-8050

### COMBINED DECLARATION AND POWER OF ATTORNEY FOR PATENT AND DESIGN APPLICATIONS

As a below named inventor, I hereby declare that, my residence, post office address and citizenship are as stated next to my name; that I verily believe that I am the original, first and sole inventor (if only one inventor is named below) or an original, first and joint inventor (if plural inventors are named below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

| nsert Title:   | ELASTOMER MATERIA  | ALS WITH IMPR  | OVED CATALYST COM  | PONENT   |   |  | <del></del>  |
|--|--|--|--|--|---|--|--|
| fill in Appropriate information -                    | the specification of which<br>the specification wa   | is attached hereto<br>s filed on   | . If not attached hereto,  |  |   |  | as   |
| or Use Without                                       | United States Appli  | cation Number  |  |  | <del> </del>  | ( C 1; - 1.1   | :  |
| Specification<br>Attached:                           | and amended on   | s filed on Santa   | mber 1 2000  |  |   | (if applicabl  | e) and/or  |
| ttuenea.   | International Applic   | ation Number P   | mber 1, 2000<br>CT/EP00/08568  |  |   |  | and was  |
| * <sub>34</sub>                                      | amended on _ Aug   | ust 2, 2001  |  |  |   | (ıf ap   | plicable)  |
|  | any amendment referred to a cknowledge the of I do not know and of patented or described in a that the same was not in not been patented or mac States of America on an at this application, and that States of America prior to | to above luty to disclose info not believe the suny printed publica public use or on selection of application filed by no application for othis application beging priority benefit diana discontinuous discontinuou | ale in the United States c<br>y me or my legal represe<br>r patent or inventor's cer<br>y me or my legal represe<br>s under Title 35, United<br>fied below any foreign a | al to patentability a<br>used in the United<br>re my or our invent<br>f America more the<br>sued before the da<br>ntative or assigns<br>ufficate on this inventatives or assigns,<br>States Code, §119(  | as defined in Title 37, Co<br>I States of America before<br>tion thereof or more than<br>an one year prior to this<br>te of this application in<br>more than twelve month<br>ention has been filed in<br>, except as follows<br>a)-(d) of any foreign app | ode of Federal Regu<br>ore my or our inventa-<br>one year prior to the<br>application, that the<br>any country foreign<br>s (six months for deany country foreign<br>any country foreign | lations, §1 56 tion thereof, consistency of the application in the transfer of the Unite esigns) prior to the Unite unite of the Unite of the Unite of the Unite of the Uniterity of the Uniterit |
|  | Prior Foreign Applicat   | •  | ,  |  |   | Priority   | Claimed  |
| Insert Priority                                      |  | _  |  | Santamba   | - 6 1000  |  |  |
| Information:   | 199 42 459.4<br>(Number)   | Germany<br>(Country)   |  | (Month/Day   | r 6, 1999   | ⊠<br>Yes   | □<br>No  |
| (if appropriate)                                     | (ivaniber)   | (Country)  |  | (terontin 15ay)  | rear ined)  | -  |  |
|  |  |  |  |  |   |  |  |
|  | (Number)   | (Country)  |  | (Month/Day   | (Year Filed)  | Yes  | No   |
|  |  |  |  |  |   |  |  |
|  | (Number)   | (Country)  |  | (Month/Day   | /Year Filed)  | Yes  | No   |
|  |  |  |  |  |   |  |  |
|  | (Number)   | (Country)  |  | (Month/Day   | /Year Filed)  | Yes  | No<br>No   |
|  | I hereby claim the benefi  | t under Title 35, U  | Inited States Code, §119   | e) of any United St  | ates provisional applicat   | ions(s) listed below   | ·.   |
| Insert Provisional Application(s): (if •••)          | (Application Number)   |  |  | (Filing I  | Date)   |  | <del></del>  |
|  | (Application Number)   |  |  | (Filing I  | Date)   |  |  |
|  | All Foreign Applications Date of This Application  |  | atent or Inventor's Certi  | ficate Filed More t  | han 12 Months (6 Mont   | hs for Designs) Pri  | or to the Filir  |
|  | Country  |  | Application Number   |  | Date of Filing (Month   | h/Day/Year)  |  |
| Insert Requested<br>Information:<br>(if appropriate) |  |  |  |  |   |  |  |
|  | I hereby claim the benefithe subject matter of ea<br>provided by the first par<br>patentability as defined<br>and the national of PC F   | ch of the claims of agraph of Title 35 in Title 37, Code of  | of this application is no United States Code, §  | disclosed in the place of the p | prior United States and/<br>te the duty to disclose in  | or PC L application<br>formation which is  | in the mann<br>material to the   |
| Insert Prior U.S. Application(s): (if any)           | (Application Number)   | <del></del>  | (Filing Date)  |  | (Status - patented, pe  | nding, abandoned)  |  |
| Page 1 of 3<br>(Rev. 12/19/01)                       | (Application Number)   |  | (Filing Date)  |  | (Status - patented, po  | nding, abandoned)  |  |

Attorney Docket No. 0475-205P

I hereby appoint the practitioners at CUSTOMER NO. 2292 as my attorneys or agents to prosecute this application and/or an international application based on this application and to transact all business in the United States Patent and Trademark Office connected therewith and in connection with the resulting patent based on instructions received from the entity who first sent the application papers to the practitioners, unless the inventor(s) or assignee provides said practitioners with a written notice to the contrary:

Send Correspondence to:

#### BIRCH, STEWART, KOLASCH & BIRCH, LLP or CUSTOMER NO

P.O. Box 747 • Falls Church, Virginia 22040-0747

Telephone: (703) 205-8000 • Facsimile: (703) 205-8050

PLEASE NOTE: YOU MUST COMPLETE THE FOLLOWING:

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

| Cutt Manage of Firm  |  |   |                       |                                   |  |  |
|--|--|---|-----------------------|-----------------------------------|--|--|
| Full Name of First or Sole Inventor: asent Name of Inventor                | GIVEN NAME/FAMILY NAME   | INVENTOR'S SIGNATURE  |                       | DATE*                             |  |  |
| nsert Date This<br>Document is Signed                                      | Joachim ZECH   | hogdin Lier   |                       | 18.03.2002                        |  |  |
| nsert Residence<br>Insert Citizenship →                                    | Residence (City, State & Country)  | V   | CITIZENSHIP           |                                   |  |  |
| issert Catzensiap -  | Kaufering GERMANY  |   | German                |                                   |  |  |
| nsert Post Office Address →  | MAILING ADDRESS (Complete Street Address including City, State & Country) Kolpingstrasse 61c, D-86916 Kaufering GERMANY  |   |                       |                                   |  |  |
|  |  |   |                       |                                   |  |  |
| ne of Second   | GIVEN NAME/FAMILY NAME   | INVENTOR'S SIGNATURE  |                       | DATE*                             |  |  |
| see above  | Gunther ECKHARDI   | Junther Ect   | Lordy                 | 13.03.2002                        |  |  |
| $\propto$  | Residence (City, State & Country)  |   | CITIZENSHIP           |                                   |  |  |
|  | Bad Duerrenberg GERMANY  | <del>-</del> X  | German                |                                   |  |  |
|  | MAILING ADDRESS (Complete Street Address inclu   |   | 1                     |                                   |  |  |
| OdF-Strasse 22, D-06231 Bad Duerrenberg GERMANY                            |  |   |                       |                                   |  |  |
| Full Name of Third<br>Inventor, if any:                                    | GIVEN NAME/FAMILY NAME   | INVENTOR'S SIGNATURE  |                       | DATE*                             |  |  |
| see above  | Cornelia <u>FÜHRER</u>   | Cornelia Führer   |                       | 25.03.02                          |  |  |
| ح م  | Residence (City, State & Country)  |   | CITIZENSHIP           |                                   |  |  |
| 0  | Wertach GERMANY  |   | German                | Ź                                 |  |  |
|  | MAILING ADDRESS (Complete Street Address inclu   | uding City, State & Country)  | <del></del>           |                                   |  |  |
|  | Schimmelreiterweg 4, D-87497 Wertach GERMANY   |   |                       |                                   |  |  |
|  |  |   |                       |                                   |  |  |
| Full Name of Fourth Inventor, if any:                                      | GIVEN NAME/FAMILY NAME   | INVENTOR'S SIGNATURE  |                       | DATE*                             |  |  |
| Full Name of Fourth<br>Inventor, if any:<br>. see aboye                    | GIVEN NAME/FAMILY NAME  Bernd CANCNUS  | INVENTOR'S SIGNATURE  | ~/                    |                                   |  |  |
| Full Name of Fourth Invenior, if any: . see aboyled.                       | Y  | INMENTOR'S SIGNATURE  | CITIZENSHIP           | 26.03.2007                        |  |  |
| Full Name of Fourth Invenior, if any: . see aboye                          | Bernd GANGNUS  | INVENTOR'S SIGNATURE  | CITIZENSHIP<br>German | 26.03.2007                        |  |  |
| Full Name of Fourth<br>Invemor, if any:<br>. see about                     | Bernd GANGNUS  Residence (City, State & Country)   | 1500-cl 6309  |                       | 26.03.2007                        |  |  |
| Full Name of Fourth<br>Inventor, if any:<br>. see aboyle                   | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  | uding City, State & Country)  |                       | 26.03.2007                        |  |  |
| Full Name of Fifth Inventor, if any: . see about                           | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included)  | uding City, State & Country)  |                       | 26.03.200 7                       |  |  |
| Invenior, if any:  see abole  Full Name of Frûth                           | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included Moosweg 2b, D-82346 Andechs GERMANY   | uding City, State & Country)  |                       | 26.03.2007                        |  |  |
| Invenior, if any:  see abole  Full Name of Frûth                           | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address includes and the S | uding City, State & Country)  |                       | 26.03.2007<br>DATE*<br>22.03.2002 |  |  |
| Invenior, if any:  see abole  Full Name of Frûth                           | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address includence of the Country)  Moosweg 2b, D-82346 Andechs GERMANY  GIVEN NAME/FAMILY NAME  Andreas ROMBACH   | uding City, State & Country)  | German                | 26.03.2007<br>DATE*<br>22.03.2002 |  |  |
| Invenior, if any:  see abole  Full Name of Frûth                           | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included and State Ad | INVENTOR'S SIGNATURE  | CITIZENSHIF           | 26.03.2007<br>DATE*<br>22.03.2002 |  |  |
| Invenior, if any:  see abole  Full Name of Frûth                           | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included and Street Address includ | INVENTOR'S SIGNATURE  Unding City, State & Country)   | CITIZENSHIF           | 26.03.2007<br>DATE*<br>22.03.2002 |  |  |
| Invenior, if any:  see abole  Full Name of Frûth                           | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included and the state of the street Address included and the state of the stat | INVENTOR'S SIGNATURE  Unding City, State & Country)   | CITIZENSHIF           | DATE* 22.03.2002                  |  |  |
| Full Name of Fifth Inventor, if any:  see above                            | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included and the country)  GIVEN NAME/FAMILY NAME  Andreas ROMBACH  Residence (City, State & Country)  Herrsching GERMANY  MAILING ADDRESS (Complete Street Address included and the country)  Weinhartstrasse 3, D-82211 Herrsching GIVEN NAME/FAMILY NAME  Oswald GASSER   | INVENTOR'S SIGNATURE  Unding City, State & Country)  unding City, State & Country)  ing GERMANY   | CITIZENSHIF           | DATE* 22.03.2002                  |  |  |
| Full Name of Fifth Inventor, if any:  Full Name of Sixth Inventor, if any: | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included and the country)  GIVEN NAME/FAMILY NAME  Andreas ROMBACH  Residence (City, State & Country)  Herrsching GERMANY  MAILING ADDRESS (Complete Street Address included and the country)  Weinhartstrasse 3, D-82211 Herrsching GIVEN NAME/FAMILY NAME  | INVENTOR'S SIGNATURE  Unding City, State & Country)  unding City, State & Country)  ing GERMANY   | CITIZENSHIF           | 26.03.2007<br>DATE*<br>22.03.2002 |  |  |
| Full Name of Fifth Inventor, if any:  Full Name of Sixth Inventor, if any: | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included and the country)  GIVEN NAME/FAMILY NAME  Andreas ROMBACH  Residence (City, State & Country)  Herrsching GERMANY  MAILING ADDRESS (Complete Street Address included and the country)  Weinhartstrasse 3, D-82211 Herrsching GIVEN NAME/FAMILY NAME  Oswald GASSER   | INVENTOR'S SIGNATURE  Unding City, State & Country)  unding City, State & Country)  ing GERMANY   | CITIZENSHIF<br>German | DATE* 22.03.2002                  |  |  |
| Full Name of Fifth Inventor, if any:  Full Name of Sixth Inventor, if any: | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included and Street Address includ | INVENTOR'S SIGNATURE  uding City, State & Country)  ing GERMANY  INVENTOR'S SIGNATURE   | CITIZENSHIF German    | DATE* 22.03.2002                  |  |  |
| Full Name of Fifth Inventor, if any:  Full Name of Sixth Inventor, if any: | Bernd GANGNUS  Residence (City, State & Country)  Andechs GERMANY  MAILING ADDRESS (Complete Street Address included and the country)  GIVEN NAME/FAMILY NAME  Andreas ROMBACH  Residence (City, State & Country)  Herrsching GERMANY  MAILING ADDRESS (Complete Street Address included and the country)  Weinhartstrasse 3, D-82211 Herrschild GIVEN NAME/FAMILY NAME  Oswald GASSER  Residence (City, State & Country)  Seefeld GERMANY   | uding City, State & Country)  University State & Country)  University State & Country)  University State & Country  University State & Country  University State & Country) | CITIZENSHIF German    | DATE* 22.03.2002                  |  |  |

Page 2 of 3 (Rev. 12/19/01)

<sup>\*</sup>DATE OF SIGNATURE

Attorney Docket No.0475-205P

| and the Commence of the                               |   |                              |             |                |  |
|---|---|------------------------------|-------------|----------------|--|
| ull Name of Seventh<br>Inventor, if any,<br>see above | GIVEN NAME/FAMILY NAME                        | INVENTOR'S SIGNATURE         |             | DATE*          |  |
| """"""""""""""""""""""""""""""""""""""                | Ihomas KLETTKE                                | Hounce White                 |             | 20.03.7007     |  |
| • '   | Residence (City, State & Country)             |                              | CITIZENSHIP | 01700          |  |
|   | Schondorf GERMANY,                            |                              | German      |                |  |
|   | MAILING ADDRESS (Complete Street Address incl | uding City, State & Country) |             |                |  |
| ·   | Landsberger Strasse 73, D-86                  | 938 Schondorf GERMANY        |             | 10/0           |  |
| Il Name of Eighth                                     | GIVEN NAME/FAMILY NAME                        | INVENTOR'S SIGNATURE         |             | DATE*          |  |
| 300 3000 0  | Erich WANEK                                   | Leich Would                  | _           | March 18, 2002 |  |
| •   | Residence (City, State & Country)             | <u> </u>                     | CITIZENSHIP | 1              |  |
|   | Kaufering GERMANY DEX                         |                              | -German- /  | AUSTRIAN       |  |
| ` _   | MAILING ADDRESS (Complete Street Address incl | uding City, State & Country) | ·           |                |  |
|   | Eschenstrasse 15, D-86916 Kauferin            | g GERMANY                    |             | 9 9            |  |
|   |   |                              |             |                |  |